

# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Production of Terpenic Esters

We, A BOAKE, ROBERTS AND COMPANY, LIMITED, a British Company of, Carpenters Road, Stratford, London E.15 do hereby declare the invention, for which we pray  
5 that a Patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to the production  
10 of certain terpenic esters, namely esters of the related terpene alcohols; linalol, geraniol and nerol.

It is known to prepare linalyl, geranyl and neryl esters from  $\beta$ -pinene by a synthetic route which involves thermal isomerisation of  $\beta$ -pinene to produce myrcene; addition of hydrogen halide thereto in the presence of copper catalysts to produce allylic terpenic halides, e.g. linalyl,  
15 geranyl and neryl halides; followed by their conversion to the desired esters, often by reaction with a carboxylate salt in the presence of the free carboxylic acid as reaction medium. It has also been proposed to  
20 prepare the mixture of these allylic halides by hydro-halogenation of ocimene which may be obtained by careful thermal isomerisation of  $\alpha$ -pinene. However, each of these routes involves a two step conversion of  
25 myrcene or ocimene to the desired linalyl, geranyl and neryl esters and a method for the direct hydrocarboxylation of myrcene or ocimene is a desirable concept which has not hitherto been satisfactorily realised.  
30 In U.S.P. 2,467,330 (published 1949) Milas described the reaction of myrcene and ocimene with water, carboxylic acids or alcohols to produce respectively linalol and geraniol or esters or ethers thereof, the  
35 reaction being carried out in the presence of an acid catalyst and a phenolic antioxidant. Moreover, the results show that the production of linalyl esters is apparently

more favoured than the corresponding geranyl and neryl isomers. The acid catalysts specified are all strong acids and they are stated to be required in an amount varying from 1 to 10% or more, based on the weight of the myrcene or ocimene. Earlier work on the direct hydration of myrcene and ocimene had likewise been reactions carried out in the presence of significant amounts of a strong acid and only low yields of product had been obtained. Attempted repetition of the work of Milas (as illustrated hereinafter) has indicated that esters of linalol, geraniol and nerol result only in very small amounts from the procedures advocated by him for the direct hydrocarboxylation of myrcene, the chief products being terpinyl and myrcenyl esters. It will be appreciated that since modern analytical methods were not available to Milas and earlier workers they may have been misled in their identification of the products obtained.

It has now surprisingly been found that very useful yields of the desired terpenic esters are obtained if the general hydrocarboxylation procedure of Milas is modified so that it is carried out in the absence of the strong acid. In fact we have found that the presence of more than  $10^{-3}$  moles of strong acid per mole of myrcene will markedly reduce the yield of the desired esters. We have further found that the ester product of such a reaction in the absence of strong acid is predominantly a mixture of the geranyl and neryl esters and that only a small proportion of the linalyl ester is formed; this result is also contrary to the teaching of Milas.

Accordingly, the present invention provides a process for the production of terpenic esters which comprises reacting myrcene with an aliphatic carboxylic acid hav-

ing at least two carbon atoms in the presence of an antioxidant and in the substantial absence of oxygen and strong acids.

The myrcene reactants may be obtained 5 from the thermal isomerisation of  $\beta$ -pinene. The myrcene need not be pure for present use, but should preferably be relatively free of other hydrocarbons with conjugated unsaturation. The commercially-10 available material known as "myrcene-80" which contains 80% myrcene with the balance being mainly dipentene is particularly suitable.

The aliphatic carboxylic acid reactant 15 must have at least two carbon atoms since formic acid has been found to be unsuitable. It may conveniently have as many as 20 carbon atoms, but acids with 2 to 6 carbon atoms are preferred, particularly 20 acetic acid. Dicarboxylic acids may also be employed if desired, but acids containing electron withdrawing substituents, such as halogen atoms and nitrile groups, on the  $\alpha$  or  $\beta$  carbon atoms are best avoided as 25 they tend to function as the strong acid which may only be present in very small amounts in the process of the invention. The nature of the carboxylic acid reactant is often immaterial since the ester products 30 are usually used as intermediates for the production of the perfumery alcohols geraniol, nerol and linalol. However, a few of the esters, especially the acetates, find direct use in some perfumery applications. 35 Water need not be excluded from the reaction mixture, but the amount thereof should not exceed 70% by weight of the reaction mixture. The acid reactant is normally present in considerable stoichiometric excess 40 to the myrcene. For example, a molar ratio may be as high as 20 : 1, though a ratio of from 7 : 1 to 12 : 1 is preferred.

The reaction is essentially carried out in 45 the presence of an antioxidant and the substantial absence of oxygen in order to overcome the tendency of the terpenic hydrocarbon to undergo polymerisation or oxidation reactions. The antioxidant employed is an oxygen-scavenger and phenolic anti-50 oxidants are preferred. Other possible antioxidants are tertiary phosphite esters and organic phosphines and sulphides. Examples of antioxidants include: hydroquinone, catechol, thymol, tert.-butyl catechol, tert.-butyl-cresol, butylated hydroxyanisole, 2,6-di-tert.-butyl-4-methyl phenol, 2,4-di-tert.-butyl-6-methyl phenol and methylene bis-phenols with methyl and/or tert.-butyl substituents. The antioxidant is 55 desirably present in an amount of at least 60 0.1% based on the weight of the reaction mixture, but an amount of 0.5 to 1.5% is preferred and the amount can be as high as 5% on the above stated basis. The reaction 65 is usually carried out in a closed ves-

sel in an inert atmosphere, for example nitrogen or carbon dioxide.

As hereinbefore stated, the present process is preferably carried out in the complete absence of strong acids, but it is most 70 desirable that the total amount of strong acid should not exceed  $10^{-3}$  mole per mole of myrcene. By strong acid in the present context is meant one of the strength of a mineral acid, or a Lewis acid such as zinc 75 chloride, aluminium chloride or boron trifluoride, which of course excludes under this heading the carboxylic acid present as reactant. Preferably there will be present no more than the maximum specified amount 80 of an acid having a dissociation constant  $K_a$  greater than  $5 \times 10^{-3}$ , for example such acids as sulphuric, p-toluenesulphonic or phosphoric acid.

In the process of the invention the myrcene is contacted with the carboxylic acid. The mixture is usually heated to a temperature of 50 - 250°C, but such that the reactants are preferably maintained in the liquid phase. No reaction diluent is normally employed but a mutual solvent which can be the anhydride of the carboxylic acid reactant, may be present if desired. In any case the preferred reaction temperature appears to be 10 - 20°C below the reflux temperature of the reaction mixture and to promote the reaction under such conditions it may be desirable to carry it out under super-atmospheric pressure. Thus, often the reaction is carried out at a temperature 95 of from 100-150°C.

After the conclusion of the reaction, the progress of which may be followed by periodic or continuous analysis of the reaction mixture or a sample thereof, for example by spectroscopic methods, the products are separated by known methods. For instance, the terpenic esters may be separated from excess acid and unreacted hydrocarbon by water and ether extraction, 110 if necessary with previous neutralisation of the excess acid. Residual acid and unreacted terpene hydrocarbon can also be removed by appropriate distillation of the crude reaction mixture. The product is 115 mainly a mixture of terpenic esters in which it is found the geranyl and the geometric isomeric neryl esters greatly predominate. This mixture may be separated by conventional fractional distillation techniques. The esters may be saponified, if desired, to obtain the free terpenic alcohols.

The failure of the prior art process of Milas is illustrated by the following experiment.

Myrcene (136 g.), glacial acetic acid (480 g.), p-toluene-sulphonic acid (9 g.), hydroquinone (1.5 g.) and water (18 g.) were stirred for seven hours at 45 - 50°C under an atmosphere of carbon dioxide. At the 130

end of the reaction time the product was poured into water (600 g.) and the resulting oil was washed once with water, dried over potassium carbonate and distilled. The product was analysed by gas-liquid chromatography and shown to contain no linalol or linalyl acetate. The three main products were terpinyl and myrcenyl acetates and an unidentified alcohol. Only traces of geranyl and neryl and other acetates were found.

The invention is illustrated by the following Examples. Example 1 illustrates the relatively poor results obtained when the reaction is carried out in the presence of even a small amount ( $6 \times 10^{-4}$  mole per mole of myrcene) of a strong acid. Example 1 also shows that, even with less of the strong acid than used by Milas, the results are less satisfactory than in Example 2 which illustrates the preferred process of the invention carried out in the absence of any strong acid.

#### 25 Example 1

Myrcene (136 g.), glacial acetic acid (480 g.) dilute sulphuric acid (0.06 g.), butylated hydroxyanisole (1.0 g.), were stirred for 24 hours at 45 - 50°C. The product was worked up as in the above Experiment. Conversion was low (5%) and, of the acetates, myrcenyl (20%),  $\alpha$ -terpinyl (40%), neryl (10%) and geranyl (10%) acetates were the main products.

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#### Example 2

Myrcene (50 lbs. of 80% myrcene), glacial acetic acid (250 lbs.) and tert.-butyl catechol (0.5 lb.) were stirred at 110-120°C for 36 hours. The excess acetic acid and unchanged myrcene (25 lbs.) were removed under vacuum and a yield of 10 lbs. of acetates was obtained. About 55% of the acetates were geranyl and neryl acetates and the next two components were myrcenyl (15%) and  $\alpha$ -terpinyl (12%) acetates.

What we claim is:—

1. A process for the production of terpenic esters which comprises reacting myrcene with an aliphatic carbon carboxylic acid having at least two carbon atoms in the presence of an antioxidant and in the substantial absence of oxygen and strong acids.

2. A process according to claim 1 where- 55 in the carboxylic acid has from 2 to 6 carbon atoms.

3. A process according to any of the preceding claims wherein the carboxylic acid used has no electron withdrawing sub- 60 stituents on the  $\alpha$  or  $\beta$  carbon atoms.

4. A process according to either of claims 2 or 3 wherein the carboxylic acid is acetic acid.

5. A process according to any of the 65 preceding claims wherein the carboxylic acid : myrcene molar ratio is from 7 : 1 to 12 : 1.

6. A process according to any of the preceding claims wherein the antioxidant is 70 a phenolic antioxidant.

7. A process according to any of the preceding claims wherein the antioxidant is present in a proportion of 0.5 to 1.5% by weight of the reaction mixture. 75

8. A process according to any of the preceding claims wherein there is present no more than  $10^{-3}$  moles of an acid having a dissociation constant K. greater than 5  $\times 10^{-3}$ . 80

9. A process for the production of geranyl and neryl acetates substantially as described in either of the Examples.

10. Geranyl, neryl and linalyl esters whenever produced by a process according 85 to any of the preceding claims.

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